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Carbon: A New View of its High-Temperature Behavior

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An increasing body of research indicates that carbon can exist in a number of polymorphic "linear" forms. It is proposed that these forms occur because of a shift to triple bounding in the carbon system as temperature increases above 2600 K. It is also proposed that graphite can dissociate into triple-bonded molecules by a simple mechanism.

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CARBON: A NEW VIEW OF ITS HIGH-TEMPERATURE BEHAVIOR

The discovery of new carbon forms in 1968 by El Goresy and G. Donnay in the United States and A. M. Sladkov and Yu. P. Koudrayatsev in Russia opened a field of research that is revealing heretofore unsuspected aspects of the behavior of carbon at high temperature (1, 2). Since their discovery, these carbon forms have been studied by the Russian scientists and at The Aerospace Corporation. Otherwise, they have received little attention. The Russian work, the laser Raman results of Nakamizo and Kammereck at The Pennsylvania State University, and the work of Fryer at the University of Glasgow indicate that these carbon forms contain -C ≡ C- units probably as chains (3,4,5). Since acetylene is the high-temperature stable organic molecule, it is entirely reasonable to expect high-temperature carbon forms of this general structure. Also, from a structural point of view, diamond represents the tetrahedral form, graphite the ring form, and lonsdaleite can be considered a hybrid of these structures. However, before 1968, a polymorph representing linear carbon was not recognized. Evidently, the new forms fill this gap. The Russian scientists call these new forms "carbynes"; in this paper, they are called "linear ' rms."

If the structure of graphite is considered, it is easy to see that this structure can readily dissociate into -C ≡ C- chains. The mechanism for this is illustrated in Fig. 1, where a portion of a basal plane sheet of atoms from the graphite structure is shown. At high temperatures, a single bond can break and shift an electron into each of the adjacent double bonds. This induces another single bond to break such that one electron goes to the adjacent "free radical" double bond to form a triple bond and the other goes

to the next adjacent double bond. If the process is repeated, as shown in the figure, the entire sheet of atoms separates into $-C\equiv C-$ chains. In so doing, only electrons are shifted to rearrange bonds. Initially, the atoms move only the small distance associated with the change from double to triple bonds. As the new bonds are formed, the bond angles change to produce the linear arrangement of atoms required for $-C\equiv C-$ bonding. These chains can be stacked in a hexagonal array, as proposed by the Russian scientists, to produce the linear forms. Because the chains can be stacked in a number of ways relative to the triple bond positions, one would expect a family of linear forms to exist. This indeed appears to be the case. Our diffraction data indicate eight forms thus far and that there may be more. The Russian scientists have reported on five forms that are in very good agreement with our results (6). It may be that the linear forms are showing what could be called "linear polytypism." Although the linear forms appear to be very similar crystallographically, they show a wide range of physical properties. Some forms are very soft, whereas others are superhard; indeed, harder than cubic BN. This indicates that there must be considerable cross-bonding between chains in some cases. However, the wide range in properties requires a wide variation of the degree of cross-bonding among the various linear forms.

It has been known for several years that the rate of transformation of graphite to linear form (probably chaoite) is very slow compared with the reverse transformation. Recently, preliminary rate data have been obtained, and the ratio of the rates was found to be about 500/1, which is consistent with the mechanism proposed in Fig. 1. The transformation from linear form to graphite involves a reaction between acetylene-like molecules, which are known to react rapidly and exothermically, whereas the reverse reaction involves the breaking of single bonds as a first step and would be expected to be a much slower process.

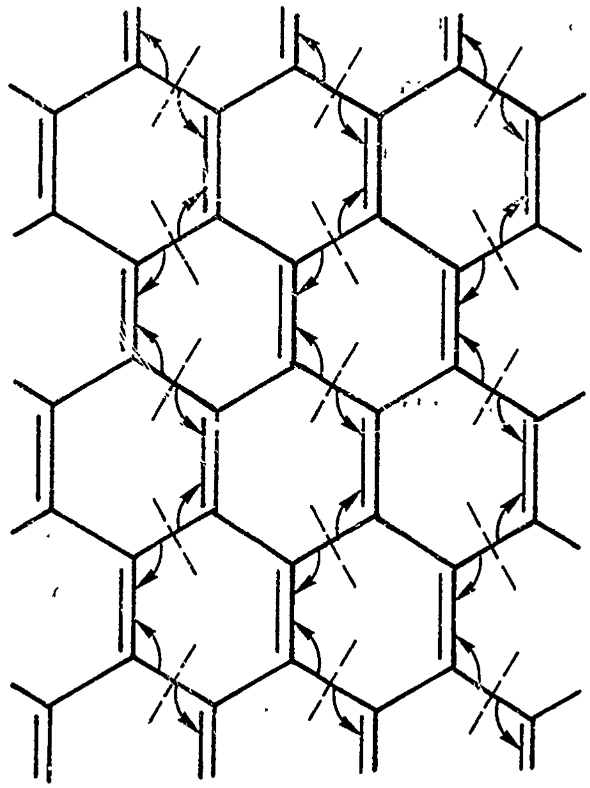

Figure 1. Mechanism for Transformation of Graphite Basal Plane Sheets of Atoms Into (-C   C-)$_n$ Chains

Because of the number, structural similarity, and unfavorable kinetics for the formation of the linear forms, studies on the phase behavior of carbon at high temperature are very difficult. However, after eight years of effort, new carbon phase diagrams, which include the linear forms, are evolving (7); the current version is shown in Fig. 2. Its important features are as follows:

1. Graphite is not stable above 2600 K at any pressure.
2. The solid-liquid-vapor triple point occurs at 3800 K and 2×10^4 Pa.
3. Linear forms are stable between 2600 and 3800 K, and their stability region extends to the diamond transition line.

Along the solid-vapor boundary, the stability range of a given linear form appears to be ~200 K; thus about six forms are expected to exist over the total range. The remaining forms, therefore, must constitute the higher pressure forms. In Fig. 2, six linear forms are shown along the solidus. Although it is easy to show that linear forms exist above 2600 K, it is very difficult to identify the equilibrium species corresponding to the various stability ranges. Consequently, future analysis may establish that the correct number is more or less than six. The transition temperatures of the first three forms are fairly well established at 2600, 2800, and 3050 K; however, except for form No. 1, which has been tentatively identified as chaoite, their identity is not known. The curve labeled JANAF gives the vapor pressure graphite would have if it were the stable form above 2600 K. Sladkov and Koudrayatsev showed that the linear forms are stable; therefore, their vapor pressures must lie below the JANAF line. Our results indicate that the equilibrium carbon form that melts to give liquid carbon is probably β carbyne (No. 6 in Fig. 2), and that the liquid is transparent, colorless, and of low emissivity (<0.02). These

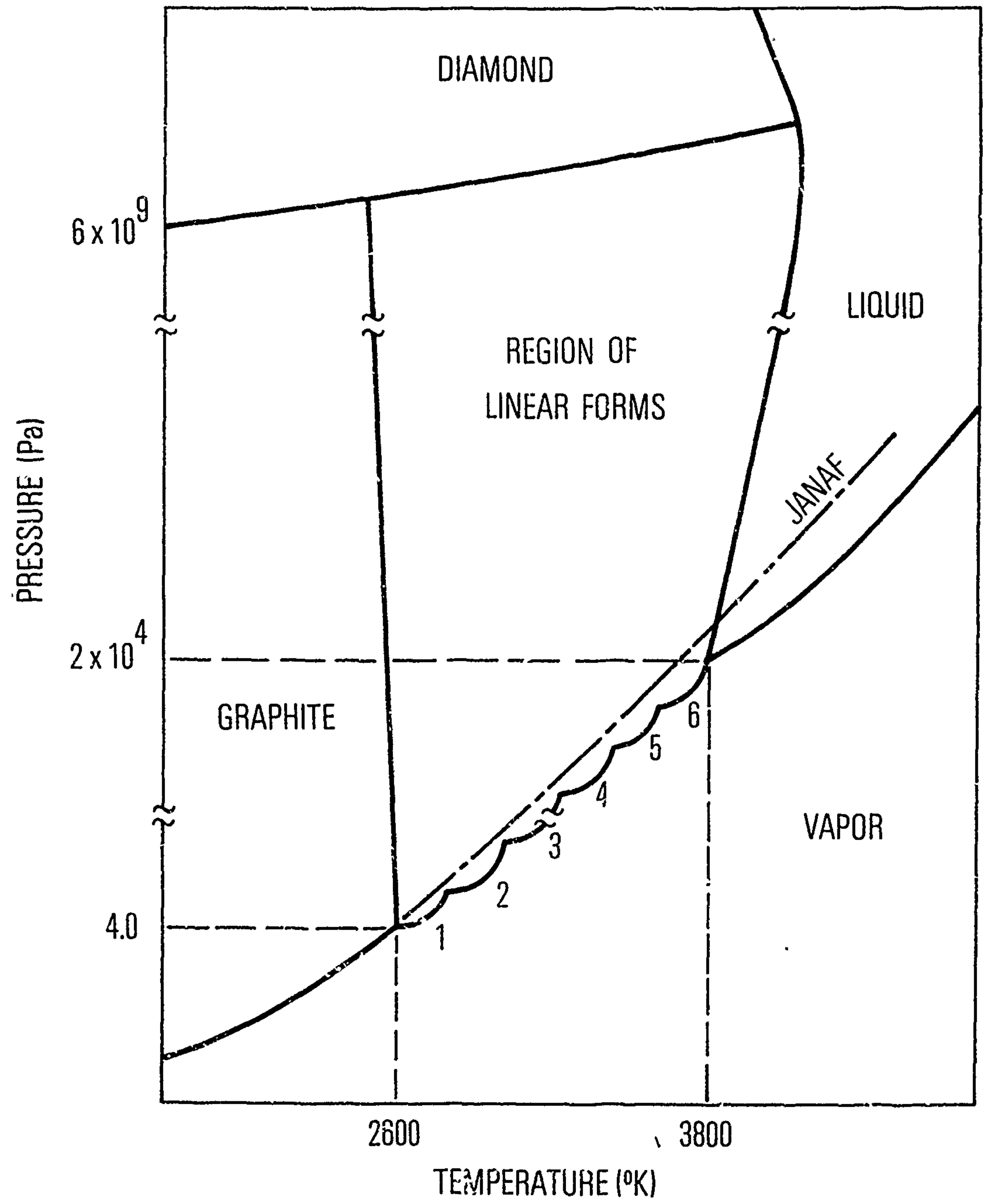

Figure 2. Proposed Form of the Carbon Phase Diagram

are the properties that a $(-C \equiv C-)_n$ liquid would have and the kind of liquid that would be expected to be in equilibrium with a $(-C \equiv C-)_m$ solid.

That carbon shifts to a triple bonded system whenever possible at high temperature is also evidenced by the C_3 emission from the gas. It is well known that the C_3 Swing's bands can be observed in emission from carbon gas at 2800 to 3000 K. However, at temperatures $\gtrsim$ 3500 K, no Swing's bands appear; this observation is supported by Null and Lozier (8) and by Howe (9). Mass spectrographic studies up to 3300 K by Milne, Beachey, and Greene (10) have shown that the C_3 concentration in carbon gas is increasing as expected. Therefore, the C_3 molecule must be shifting to another configuration that has different energy states. Swing's bands come from the double-bonded C_3 molecule C = C = C (11). As the temperature rises, it is conceivable that the configuration of the C_3 molecule could change to the triple-bonded resonance structures: $C \equiv C - C \rightleftharpoons C - C \equiv C$. This could correspond to a state slightly above the C = C = C ground state. Such a shift would account for the disappearance of the Swing's bands at high temperature, even though the C_3 concentration in the gas increases with temperature. Spectra taken during laser heating studies indicated a weak band head at 274.2 nm. This is close to a band head at 272.3 nm for acetylene and could result from emission from the triple-bonded form of C_3. It is interesting to note that the even carbon molecules, such as C_2 and C_4, cannot switch to a resonating triple-bonded configuration. Therefore, the intensity of the C_2 Swan bands should increase with temperature. This is what was observed up to ~4500 K. In this respect, it would be interesting to follow C_4 and C_5 emission intensities as a function of temperature.

Further support for a phase diagram as shown in Fig. 2 is given by some practical applications of carbon in vehicle entry hardware. From this diagram, it is possible to predict the formation and distribution of linear forms in the heated carbon structures. Also,

the phase transitions can be used to account for a wide variety of data ranging from the behavior of strain to failure versus temperature to the unusually large molar volume of the activated state for the transition of diamond to graphite. These aspects will be discussed in more detail elsewhere.

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